ASPHALTENE PRECIPITATION AND INCIPIENT FLOCCULATION IN MIXED SOLVENTS.

Simon I. Andersen,
Danish Natural Science Research Council,
H.C. Andersens Boulevard 40,
DK-1553 Copenhagen, Denmark.
and
James G. Speight,
Western Research Institute,
Laramie, WY 82071-3395

INTRODUCTION.

The presence of asphaltenes is known to have a significant effect on both processability of crude oils and the properties of asphalts (1). Indeed, the presence of asphaltenes is particularly felt when circumstances permit their separation (precipitation) from the oil medium in such a manner that the phenomenon of phase separation causes either coke formation during processing or failure of an asphalt pavement by loss of physical structure of the asphalt-aggregate system (2).

Briefly, asphaltenes are defined as the fraction of petroleum that is insoluble in an excess of a low-boiling liquid hydrocarbon, such as n-heptane, but soluble in aromatic solvents (e.g. toluene or benzene) at ambient temperatures.

Thus, there is the need to understand the stability of crude oils and this can be achieved by an investigation of asphaltene precipitation/flocculation, by titration, using solvent/non-solvent mixtures. This may give an indication of both asphaltene and maltene properties (3,4,5).

At the point of incipient precipitation, i.e. the point at which separation of asphaltenes from a crude oil becomes apparent, the precipitated material is, presumably, a conglomeration of species based on molecular size and polarity of the type that constitute the asphaltenes (6,7). This phenomenon has, however, not been addressed in any detail and is certainly worthy of investigation in order to increase the understanding of crude oil (asphaltene/maltene) relationships.

Thus, in order to investigate the mechanism of asphaltene precipitation, the change in precipitated material with changes in the non-solvent/solvent composition have been examined. Material isolated at the point of incipient precipitation was recovered and characterized by high performance liquid chromatography-size exclusion chromatography (HPLC-SEC) and diffuse reflectance spectra (DRIFT-FTIR). The possibility of determining the solubility parameter (δ) of the asphaltenes from titration and precipitation experiments was investigated.

The change in solvent composition from aromatic to aliphatic may mimic the change in oil composition during refinery, where the oil phase becomes more aliphatic with increasing conversion (8,9).

EXPERIMENTAL

Asphaltenes were precipitated by addition of 30 mL precipitant per gm oil at 20°C. Mixtures of n-heptane and toluene containing up to 40% (vol/vol) of toluene were used as the precipitant.

A modification of the asphaltene separation method (IP 143) was used as described elsewhere (10). Thus, after a 16 hr. contact time, precipitated asphaltenes were further purified by treatment with 3 x 10 mL of the appropriate solvent mixture, sonication, centrifugation (4000 rpm), and decantation.

The flocculation threshold in solvent/non-solvent mixtures was determined by measuring the light absorbance at 740 nm of the titrated solution. From a burette n-heptane was added to a stirred asphaltene or oil solution in a beaker. Asphaltene concentrations in initial solution was kept at 4 g/L. The flocculation point or threshold (FT) is the solvent composition (i.e. the volume fraction of solvent in non-solvent) where the absorbance increases rapidly. The absorbance was measured 20 min. after each addition of non-solvent, allowing equilibrium conditions to be reached; shorter time periods gave inconsistent readings.

Two commercial asphaltene solvents (methylnaphthalene oil and Basen 140/160) supplied by Preussag Erdoel und Erdgas GmbH, Hannover, Germany were also examined.

The crude oil investigated was a Kuwait oil topped at 100°C and supplied by Kuwait Petroleum Denmark A/S.

Infrared spectra were recorded using a BIO-RAD (Digilab Division) model FTS-45 Fourier Transform infrared (FTIR) spectrometer with an attachment for diffuse reflectance spectra (DRIFT) (11).

Synchronous fluorescence spectra were obtained as described elsewhere (10); asphaltenes were dissolved in mixtures of n-heptane and toluene (10-100% toluene) at a specified concentration (5 mg/L). No precipitation or particle formation was observed by Rayleigh scattering at 460 nm.

Size exclusion chromatography (HPLC-SEC) analysis was performed using a Hewlett-Packard 1090 HPLC with a diode array detector (DAD) with 8 wavelengths, and a Waters R401 refractive index (RI) detector. Freshly distilled toluene was used as eluant at a flow rate of 2 mL/min at 30 C. The column was a Phenomenex 5 μm, 10^4 A, 30 cm 7.9 mm i.d. The DAD wavelengths were 305, 340, 380, 410, 420, 460, 500, and 575 nm. The injected sample concentrations were 10 g/L toluene.

RESULTS AND DISCUSSION.

In the flocculation titration experiments a difference was found for solutions of pure asphaltenes and of the original oil. The latter showed a lower flocculation threshold (0.31±0.02) in terms of toluene in n-heptane than the asphaltene solutions (0.41±0.03). This was also noted for asphaltenes precipitated under a variety of conditions. This indicates that more non-solvent is required to precipitate the asphaltenes in the presence of maltenes.

The effect of various asphaltene solvents on the flocculation threshold, using n-heptane as the non-solvent, was also examined. A comparison of the various flocculation thresholds with the effective Hildebrand solubility parameter (δ_{eff}) of the relevant solvent mixture (Table I) suggests that, although solvent-solute interactions vary, δ_{eff} is similar (16.7 MPa$^{1/2}$ ± 0.3) for all solvent systems except for 2,4-dimethylpyridine.

Immiscibility is known to occur at solubility differences between solvent and solute of ca. 3.5 to 4 MPa$^{1/2}$. Hence the solubility parameter of the precipitated material can be estimated to fall within the range 20.2-20.7 MPa$^{1/2}$ which is in accordance with previous work (12,13).

Using the data further, it is predictable that there will be no precipitation of material above a flocculation threshold of 0.33 (δ_{eff} = 16.2 MPa$^{1/2}$) for the total oil (Figure 1).

As expected the amount of precipitated material decreased with increasing content of toluene in heptane. Purification of the raw precipitate from the 40% toluene/heptane precipitant, led to the recovery of a toluene insoluble solid (0.26 %) which was partially soluble in methylene chloride.

It is possible that this material could be finely-suspended mineral matter which acts as nuclei for the part of the asphaltene, presumably the most polar, and which forms part of the initial precipitate with highly polar species (14). Without any such effect, these species would remain in "solution" and be precipitated in the usual manner. Investigations using FTIR spectroscopy and HPLC-SEC revealed that, at least part of, the material was low molecular weight and reacted through hydrogen bonding. In the presence of the remaining asphaltene material, the sample was soluble suggesting some rearrangement of the molecular interactions during the removal of lower molecular weight (polar) asphaltene species, which could indicate a co-solvency effect through association.

The material precipitated from n-heptane to toluene insolubles may have a δ-distribution between 19 and above 22 MPa$^{1/2}$ which is in disagreement with the data from the titration experiments which give an upper limit of 20.7 MPa$^{1/2}$, and hence were not able to predict the presence of toluene insoluble material. One titration experiment using 2,4-dimethylpyridine showed a flocculation threshold of 0.42 (18.3 MPa$^{1/2}$) indicating an upper limit of 22.3 MPa$^{1/2}$.

A reasonable explanation of this phenomenon is that asphaltenes associate less in pyridine (15). Hence, the interactions leading to dispersion of the least soluble part are not present, and the compounds behave as single molecular entities. The latter is possible as the asphaltene concentration of this sample is below the critical micelle concentration (4.32 g/L) at the beginning of the titration (16). Hence, if solubility parameters are determined from titration experiments, the data are relative to the conditions such as solvent system and equilibrium time.

Data from the FTIR spectra imply that the chemical nature of the precipitate changes gradually at first but become more obvious as the incipient precipitation conditions are approached. Thus, the relative content of long chain paraffinics (720 cm^{-1}) increases as do the content of carboxylic acid functions (1730-1700 cm^{-1}). The latter increases rapidly above a concentration of 25% toluene. This indicates that the the least soluble part, i.e. "hard core asphaltenes", which precipitates first are highly polar and contain long alkyl chains.

According to the group contribution approach for solubility parameter (δ) calculation, an increase in molecular weight does not strictly imply an increase in the magnitude of δ since long chain paraffin systems have low δ values (17). Hence, the precipitation may be governed by molecular weight differences between the solvent and the solute.

HPLC-SEC investigations showed that higher concentrations of toluene in the precipitant lead to shorter peak retention time, and changes take place on the low molecular weight side of the eluted profile. The largest change in profiles was seen when going from pure heptane to a mixture containing 10% toluene. The n-heptane asphaltenes had a close to bimodal profile where as for 10% (or higher amounts) of toluene, the profile is a single tailing peak indicating

that the incremental material, soluble in toluene/heptane but insoluble in heptane, is composed of lower molecular weight species. This suggests that asphaltenes may be composed of different molecular weight types as suggested from fractionation studies (18,19,20,21,22).

The relative change in chemical types was then investigated by a study of the ratios of total areas under the chromatograms obtained at different diode array detector (DAD) wavelengths (Figure 2). The amount of larger chromophores increases relatively as the toluene content in the precipitant rises. DAD and refractive index (RI) signals are different but the overall conclusion the same.

Hydrogen bonding is involved, to some extent, in asphaltene association and dispersion (23). Indeed, an examination of the FTIR spectra, particularly in the range 3100-3700 cm^{-1}, showed that the main change in the nature of the precipitates from that obtained with pure heptane to that obtained with a 40% solution of toluene in heptane, is the occurrence of less hydrogen-bonded structures.

In the spectrum of the precipitate from the "40% toluene" mixture, distinct, relatively large, bands for free hydroxyl and carboxylic hydroxyl are found. In the presence of the co-precipitated resin-type material these bands are extremely weak, indicating that dispersion of any toluene insoluble material may take place through association with the co-precipitate. A similar concept has been proposed for resin-asphaltene interaction (24). Co-precipitated material was in all samples of lower molecular weight.

In order to investigate the interactions occurring in solution synchronous fluorescence spectra were recorded in mixtures of n-C7 and toluene with toluene volume fractions (ϕ) from 0.1 to 1. Hence the entire range from total dissolution to flocculation conditions passing the previously reported (25) critical micelle concentration limit at $\phi = 0.68$. The asphaltene used was a n-octane insoluble, precipitated at 43°C.

No large changes occurred in the spectra with increasing toluene content, although the polarity of the solvent increases, which based on simple compounds should lead to peak shifts to longer wavelengths. The relative intensity of three peaks at 360, 395, and 460 nm was examined representing increasing molecular complexity (10). These results indicates a general blue shift of the intensities. If asphaltene molecules were associating a red-shift would be expected. That no interactions occurs may be caused by the very low concentration of 5 mg/L toluene. According to the solvent shell theory, asphaltenes will be dispersed as long as sufficient dispersion agent is present to form the so called solvate layer around the asphaltenes (26). This may also imply a concentration effect that can affect the titration and precipitation experiments.

CONCLUSIONS.

Discrepancies between methods (equilibrium precipitation and flocculation titration) employed to determine the incipient precipitation of asphaltenes have been found and may be related to slow kinetics of precipitation (27).

Solubility parameters of asphaltenes can be measured by the titration method but relative to the experimental parameters such as time, solvent and solute (asphaltene or oil) concentration. The recovery of a toluene insoluble fraction from a toluene soluble fraction shows the complexity of the asphaltene aggregation during precipitation. Evidence of rearrangements of molecular interactions is suggested.

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Table I: Flocculation thresholds Kuwait petroleum asphaltenes in volume fraction of solvent in n-heptane.

| Solvent | Asphaltenes (%) | | $\delta*$ | $\delta_{eff}*$ |
| | C5** | C6*** | | |
	Flocculation threshold			
Toluene	0.34	0.38	18.2	16.3
Quinoline	0.24	-	22.0	16.9
Methylnaphthalene oil	0.29	-	20.3	16.8
Basen 140/160	-	0.36	19.8	16.9
2,4-dimethylpyridine	0.43	0.42	22.2	18.3

* $MPa^{1/2}$.
**   C5: pentane asphaltenes, yield: 21%
***   C6: hexane asphaltenes, yield: 18%
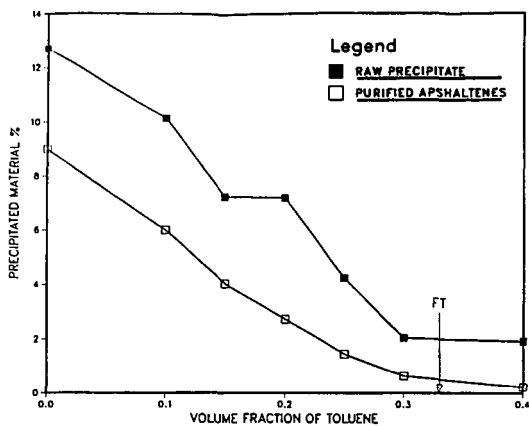$\delta_{eff} = \Sigma \phi_i \delta_i$

Figure 1. Amount of precipitated asphaltenes (raw and purified) versus volume fraction of toluene in n-heptane precipitant.
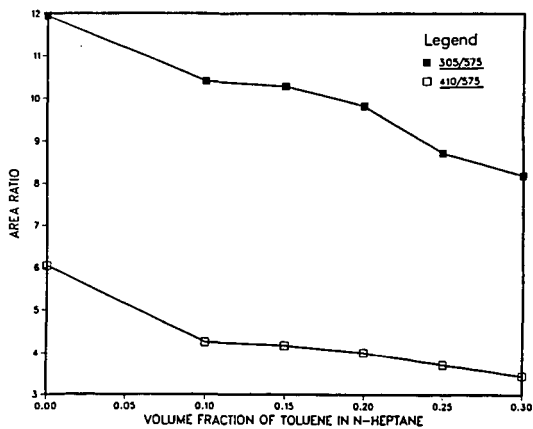

Figure 2. HPLC-SEC Peak area ratios of various detector wavelengths versus volume fraction of toluene in n-heptane precipitant. 305/575 nm and 410/575 nm.